



Effect of Cu content on the catalytic activity of CuSiBEA zeolite in the SCR of NO by ethanol: Nature of the copper species

Janusz Janas^{a,**}, Jacek Gurgul^a, Robert P. Socha^a, Stanisław Dzwigaj^{b,c,*}

^a Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Kraków, Poland

^b UPMC Univ Paris 6, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, 75252 Paris Cedex 05, France

^c CNRS, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, 75252 Paris Cedex 05, France

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ABSTRACT

The effect of Cu content on the catalytic activity of Cu_xSiBEA zeolites in the selective catalytic reduction (SCR) of NO by ethanol is investigated. The Cu_xSiBEA zeolites ($x = 0.3, 1.5$ and 3.3 Cu wt%) are prepared by a two-step postsynthesis method which allows to control the introduction of copper into BEA zeolite and thus to obtain catalysts with isolated tetrahedral Cu(II) species. The incorporation of Cu into the vacant T-sites of SiBEA framework is evidenced by XRD. The presence of isolated tetracoordinated Cu(II) as the main copper species is evidenced by DR UV–vis and XPS investigations. Cu_{0.3}SiBEA, Cu_{1.5}SiBEA and Cu_{3.3}SiBEA with isolated Cu(II) species are active in SCR of NO by ethanol with the maximum NO conversion of 33%, 45.5% and 50% and selectivity towards N₂ of 90%, 97% and 75%, respectively. These results indicate that activity of Cu_xSiBEA in the SCR process increases with Cu content and the main reaction route is the reduction of NO toward N₂. The decreases of selectivity toward N₂ and increases toward NO₂ with Cu content, is probably related to formation of small amount of octacoordinated Cu(II) as suggested by XPS data. A possible pathway for the formation of tetracoordinated Cu(II) in the framework of Cu_xSiBEA is proposed.

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1. Introduction

Since the discovery in 1993 by Iwamoto et al. [1] of the remarkable activity of Cu-ZSM-5 zeolite in the selective catalytic reduction (SCR) of NO by hydrocarbons, a lot of investigations have been performed to describe the nature of the copper sites active in this process [2–13].

Usually, the transition metal ions are introduced in the extra-framework position of the zeolite structure by ion exchange method. Zeolites with transition metal ions incorporated within the framework exhibit different and interesting catalytic properties. As we have early shown for cobalt [14–16], it is possible to control the incorporation of cobalt in framework of BEA zeolite by two-step postsynthesis method and to obtain CoSiBEA catalyst active in SCR of NO.

Recently [17], we have reported that selectivity of CuSiBEA catalysts obtained by similar two-step postsynthesis method depend on the type of Cu(II) species present. It has been shown that SCR of NO by ethanol may occur on isolated lattice mononuclear Cu(II) species and the selectivity of CuSiBEA catalyst toward N₂ decrease when extra-lattice octahedral Cu(II) species occur.

Other our investigations [18], on the SCR of NO by ethanol and propane indicate that this process may occur on isolated mononuclear Cu(II) in D_{2d} -distorted tetrahedral symmetry after Al atoms have been removed from the zeolite structure, suggesting that the latter are not responsible for the high activity in SCR of NO. Thus, we have evidenced that Cu(II) ions do not need Al atoms in their environment to be catalytically active, in contrast to earlier statements [6,7]. Moreover, the lack of correlation between the activity in SCR of NO with ethanol and the oxidation of NO to NO₂ suggests that the two reactions are more competitive than sequential as already observed for FeSiBEA and CoSiBEA catalysts [19,20].

In this work, we investigate the effect of Cu content on the state of copper and its activity in SCR of NO by ethanol. The incorporation of copper in the framework sites is evidenced by XRD and the presence of tetracoordinated Cu(II) as the main copper species is shown by DR UV–vis and XPS investigations.

* Corresponding author at: UPMC Univ Paris 6, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, 75252, Paris Cedex 05, France.
Fax: +33 1 44 27 60 33.

** Corresponding author. Fax: +48 12 4 25 19 23.

E-mail addresses: ncjanas@cyf-kr.edu.pl (J. Janas), stanislaw.dzwigaj@upmc.fr (S. Dzwigaj).

The activity of Cu_xSiBEA in the SCR process increases with Cu content and the main reaction route is the reduction of NO toward N₂.

2. Experimental

2.1. Catalyst preparation

Cu_xSiBEA catalysts ($x = 0.3, 1.5$ and 3.3 Cu wt%) were prepared by the two-step postsynthesis method reported earlier [21,22]. 2 g of siliceous BEA zeolite (Si/Al > 1300), obtained by treatment of a tetraethyl ammonium (TEA) BEA zeolite (Si/Al = 11) (RIPP, China) in a 13 mol L^{-1} HNO₃ solution (4 h, 353 K), were stirred for 24 h at 298 K in aqueous solutions containing $1.5, 8$ and $19 \times 10^{-3} \text{ mol L}^{-1}$ of Cu(NO₃)₂·3H₂O. Then, the suspensions were stirred for 2 h in air at 353 K until complete evaporation of water. The solids were washed and finally dried in air at 353 K for 24 h. The solids with 0.3, 1.5 and 3.3 Cu wt% were labelled Cu_{0.3}SiBEA, Cu_{1.5}SiBEA and Cu_{3.3}SiBEA, respectively. The all samples were pale blue.

These samples were characterized by different techniques and after a particular treatment in the case of XPS described in Section 2.2.

2.2. Catalyst characterization

Chemical analysis of copper was performed at the Service Central d'Analyse, CNRS, Vernaison.

Powder X-ray diffractograms (XRD) were recorded at room temperature and ambient atmosphere on a Siemens D5000 using the CuK_α radiation ($\lambda = 154.05 \text{ pm}$).

Diffuse reflectance UV–vis–NIR (DR UV–vis–NIR) spectra were recorded at room temperature and ambient atmosphere on a Cary 5E spectrometer equipped with an integrator and a double monochromator.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a hemispherical analyzer (SES R4000, Gammatdata Scienta) using MgK_α (1253.6 eV) radiation. The power of the X-ray source was 240 W and the analyzer pass energy was 100 eV, corresponding to a full width at half maximum (FWHM) of 0.9 eV for the Ag 3d_{5/2} peak. The area of the sample analyzed was approximately 3 mm^2 . The powder samples were pressed into indium foil and mounted on a dedicated holder. The binding energy (BE) was calibrated using Cu, Au and Ag foils as references, according to ISO 15472:2001 procedure. The BE for Si, O and Cu was measured by taking the C 1s peak at 285.0 eV as internal standard.

XPS data were obtained on fresh (Cu_xSiBEA calcined in flowing air at 773 K for 3 h), used (Cu_xSiBEA after catalytic test conditioned in dry flowing air at 453 K for 3 h) and oxidized (Cu_xSiBEA after catalytic test calcined in flowing air at 773 K for 3 h) samples. Before recording of XP spectra, the catalysts were evacuated to 10^{-7} Pa in the XPS analyzer chamber. At least 30 min was required to acquire the first XP spectrum (and the following ones) with good signal/noise ratio due to the using conventional XPS system and the low concentration of copper in the samples.

All spectra were fitted with a Voigt function (a composition 70/30 of Gaussian and Lorentzian function) in order to determine the number of components under the XPS peaks. The K_{α3} and K_{α4} satellites of Cu 2p peaks were subtracted from all copper spectra by using Casa XPS software.

2.3. Catalysis measurements

The activity of catalysts in the SCR of NO by ethanol was investigated in a conventional flow Pyrex reactor with internal diameter of 10 mm coupled to an analytical system. The reaction

temperature was measured and controlled, with precision of 0.5 K, with the help of two thermocouples: first, inserted in catalyst bed and second, placed inside of electric oven.

The composition of the feed was 1000 ppm NO, 1000 ppm ethanol, the mixture of 2 vol.% O₂ in He with a catalyst volume of 1 ml (~0.52 g) and $10,000 \text{ h}^{-1}$ gas hour space velocity. The O₂ and NO were regulated by mass flow controller. Ethanol was introduced as the liquid into the He stream by means of syringe infusion pump provided with 2.5 ml Hamilton syringe and then evaporated in 25 cm long heated stainless pipe.

A gas chromatograph (CHROM-5) equipped with TCD and FID detectors was used to analyze gas-phase components. CO₂, NO and ethylene were separated with a $8 \text{ ft} \times 1/8 \text{ in.}$ nickel HayeSep R column (Alltech) at 333 K. O₂, N₂ and CO were separated on a $2 \text{ m} \times 3 \text{ mm}$ MS 5A column (Supelco) at the same temperature. Ethanol and other organic compounds (mainly ethylene, acet-aldehyde, acetic acid, acetonitrile, and – in minor quantities – esters and other hydrocarbons) were separated with a FID detector and $2 \text{ m} \times 3 \text{ mm}$ glass columns: 10% SP-1000 on 80/100 Supelcort and 10% SP-2100 on 100/120 Supelcort, heated from 333 to 393 K.

The calculations were performed with the CHROMA 2000 computer analytical program. The O₂, NO_x and CO concentrations were monitored with a GA-60 (MADUR) flue gas analyzer provided with electrochemical sensors. The NO and ethylene concentrations were additionally measured by means of a Photovac 10S50 GC with KCl–alumina column (at 313 K) provided with a photoionization detector. The presence of NH₃ was checked with a Teflon $2 \text{ ft} \times 1/8 \text{ in.}$ column filled with a Versamide active phase. In contrast, the presence, among the reaction products, of active intermediates such as HCN and HNCO was detected by a FTIR multichannel GASMET DX-4000 gas analyzer (resolution: 7.72 cm^{-1} , optical length: 500 cm, scan time 60 s).

Before catalytic tests, the samples were heated up to 523 K in oxygen/helium mixture and then NO and ethanol vapour streams were introduced. The standard conditions are: 2 h runs at 523–623 K and 1 h runs at higher reaction temperatures (NO_x and CO_x concentrations at the reactor outlet were continuously monitored for checking if pseudo steady-state conditions are established). The reaction temperature was increased every 50 K interval up to 773 K, and then lowered in the same manner to 573 K. For NO conversion or product selectivity measurements, the heating sequence was repeated to obtain real steady-state reaction conditions in the whole reaction temperature range.

All conversion and selectivity values quoted are defined and calculated in standard manner and presented in mol%. From the analytical reasons, selectivity to dinitrogen is determined as follows:

$$S_{\text{N}_2} = 100 - (S_{\text{NO}_2} + S_{\text{N}_2\text{O}} + S_{\text{NH}_3} + S_{\text{OrgN}}) (\%)$$

where: S_{NO_2} , $S_{\text{N}_2\text{O}}$, S_{NH_3} is the selectivity toward NO₂, N₂O and ammonia, respectively and S_{OrgN} is the sum of selectivities toward nitrogen-containing organic compounds.

3. Results and discussion

3.1. Incorporation of copper into the framework of dealuminated BEA

3.1.1. X-ray diffraction and FTIR spectroscopy

XRD patterns of SiBEA, Cu_{0.3}SiBEA, Cu_{1.5}SiBEA and Cu_{3.3}SiBEA typical of BEA zeolite are very similar (Fig. 1). It is shown that the crystallinity of BEA zeolite is preserved after incorporation of copper ions in dealuminated SiBEA. All samples do not show any evidence of extra framework crystalline compounds or long-range amorphization of the zeolite.

A change of the position of the narrow main diffraction peak around 2θ of 22.60° , generally taken as evidence of framework

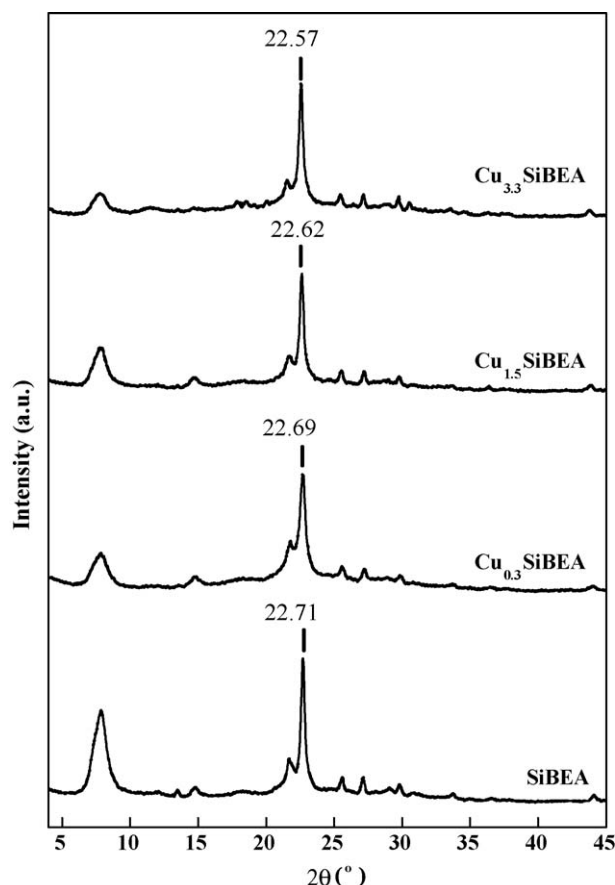


Fig. 1. X-ray diffractograms recorded at room temperature of as prepared SiBEA, $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

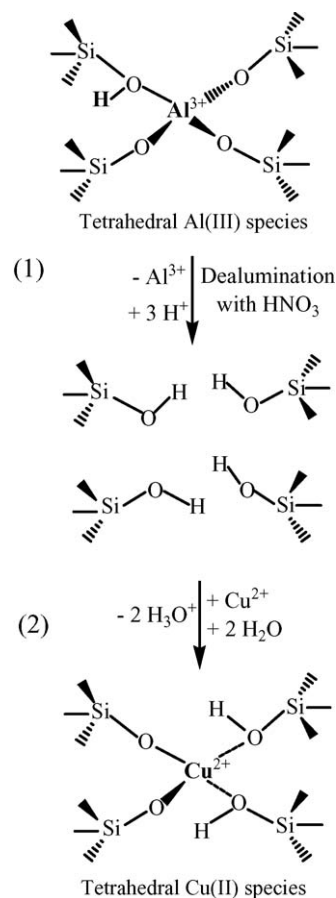
contraction/expansion of the BEA structure [23,24], from 22.71° to 22.69° , 22.62° and 22.57° (Fig. 1) after incorporation of 0.3, 1.5 and 3.3 Cu wt%, respectively indicates expansion of the matrix and suggests that copper is incorporated into the framework. The d_{302} spacing obtained from this peak increases from 3.912 Å (SiBEA) to 3.922 Å ($\text{Cu}_{0.3}\text{SiBEA}$), 3.940 Å ($\text{Cu}_{1.5}\text{SiBEA}$) and 3.942 Å ($\text{Cu}_{3.3}\text{SiBEA}$).

The treatment of AlBEA zeolite with aqueous HNO_3 solution involves the elimination of Al atoms from the framework (reaction (1) Scheme 1), as shown by the disappearance of IR bands at 3781 and 3665 attributed to AlO-H and at 3609 cm^{-1} attributed to Si-O(H)-Al groups, respectively (results not shown), in line with earlier investigations [21,22]. The appearance of narrow bands at 3736 and 3710 cm^{-1} related to isolated internal silanol groups and of a broad band at 3520 cm^{-1} due to H-bonded SiOH groups in SiBEA reveals the presence of vacant T-sites associated with silanol groups, as shown earlier [21,22,25]. The incorporation of copper leading to Cu_xSiBEA induces a reduction of intensity of these bands (results not shown), in particular this corresponding to H-bonded SiOH groups at 3520 cm^{-1} , suggesting that silanol groups of vacant T-atom sites are consumed in the reaction with copper precursor (reaction (2), Scheme 1).

3.2. Nature of the copper species in Cu_xSiBEA

3.2.1. Diffuse reflectance UV-vis-NIR spectroscopy

The DR UV-vis-NIR spectra of as prepared $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ are composed of a broad and intense band around 845 nm and another band at about 275 nm (Fig. 2). These bands may be assigned to d-d Cu^{2+} ($3d^9$) and charge transfer



Scheme 1.

(CT) $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ transitions, respectively, of isolated Cu(II) in tetrahedral coordination, taking in an account of earlier works on copper in different coordination, environment and crystal field [5,7,26–29]. The absence of UV-vis bands in the range 300–600 nm assigned to $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ CT transition and/or d-d transition of octacoordinated Cu(II) indicates that such copper are probably not present in Cu_xSiBEA samples, in line with earlier reports of Shimizu et al. [30] and Solomon et al. [31].

3.2.2. X-ray photoelectron spectroscopy

The XPS measurements were performed in the electron binding energy regions corresponding to Cu 2p, Si 2p, O 1s and C 1s core excitations. The Si 2p BE values of 103.8–104.0 eV are close to that reported earlier for zeolite-related materials [32]. The O 1s XP spectrum can be decomposed (result not shown) into three peaks with the main peak at 533.0–533.4 eV, which can be attributed to oxygen in Si-OH , in line with the results obtained for Cu-containing zeolites [32].

Table 1 shows the surface Cu/Si atomic ratio calculated from XPS data for all Cu_xSiBEA . It is identical with the bulk one for the lowest copper content ($\text{Cu}_{0.3}\text{SiBEA}$ sample) and is smaller for higher Cu content ($\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ samples). It seems that this phenomenon is related to the presence of two kinds of framework sites in BEA zeolite, as it has been recently evidenced by some of us for VSBEA system using FTIR and MQ MAS NMR [33]. It is probable that for $\text{Cu}_{0.3}\text{SiBEA}$ sample Cu ions are mainly located in the one kind of framework sites and for $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ samples Cu ions are located in the two kinds of framework sites, however mainly in the second one. It seems that the latter framework sites are present more deeply in the zeolite structure

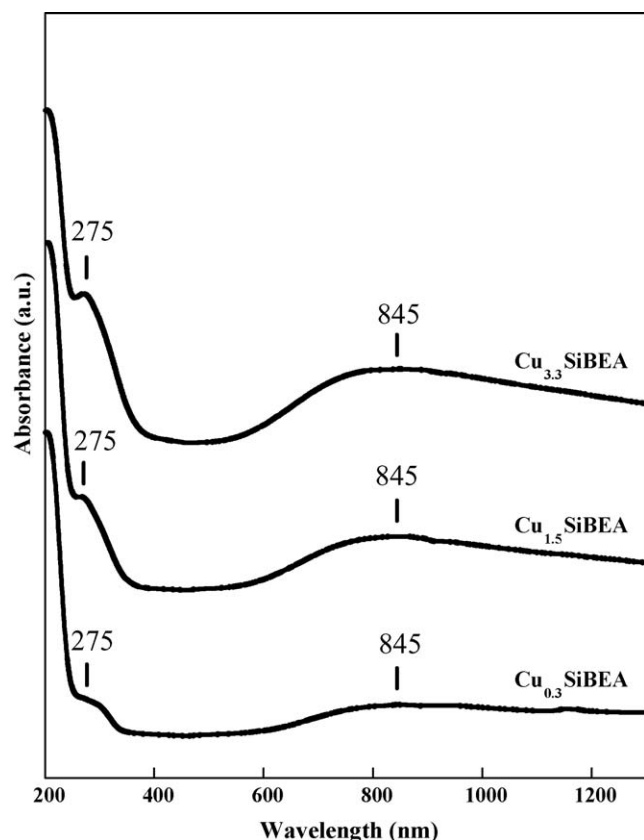


Fig. 2. UV-vis spectra recorded at room temperature of as prepared $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

than the former one and thus not all detected by XPS technique. This is probably the reason why the Cu/Si XPS ratio is comparable with bulk one for $\text{Cu}_{0.3}\text{SiBEA}$ and is smaller for $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ with higher Cu content.

Moreover, the Cu/Si ratio is not changed as a result of SCR of NO reaction (used Cu_xSiBEA) and further treatment in flowing air at 773 K for 3 h (oxidized Cu_xSiBEA) (Table 1), indicating that copper is strongly bound to the framework and do not change the location in zeolite matrix upon these processes.

The peak parameters concerning Cu 2p core level excitation are collected in Table 2 and the spectra are shown in Figs. 3–5.

Because Cu 2p_{3/2} core excitation considered alone does not allow determining the oxidation state and coordination of copper without doubt, the Cu_xSiBEA samples are characterized by using both X-ray excited Cu 2p_{3/2} and Cu L₃VV transitions. Therefore, a shake-up satellites associated with Cu 2p_{3/2} peak and a modified Auger parameter (α' , where $\alpha' = \text{BE Cu } 2p_{3/2} + \text{KE Cu L}_3\text{VV}$ and KE refers to kinetic energy) [34,35] were employed for Cu oxidation state determination.

It is important to mention here that several XPS measurements with half an hour intervals were made to verify if the copper

Table 2

XPS data of $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

Peak	Binding energy (eV)						
	$\text{Cu}_{0.3}\text{SiBEA}$		$\text{Cu}_{1.5}\text{SiBEA}$		$\text{Cu}_{3.3}\text{SiBEA}$		
	Used	Fresh	Used	Oxidized	Fresh	Used	Oxidized
Cu 2p _{3/2} (A)	933.5	933.6	933.5	933.4	933.3	933.7	933.6
Cu 2p _{3/2} (B)	937.4	937.0	936.8	936.3	936.5	936.5	936.7
KE of CuL ₃ VV ^a	913.3	913.6	913.4	913.0	913.2	913.2	913.2
$\alpha'_{(A)}$ ^b	1846.8	1847.2	1846.9	1846.4	1846.5	1846.9	1846.8

^a Kinetic energy (KE) of Auger CuL₃VV transition.

^b Modified Auger parameter = BE Cu 2p_{3/2} + KE CuL₃VV.

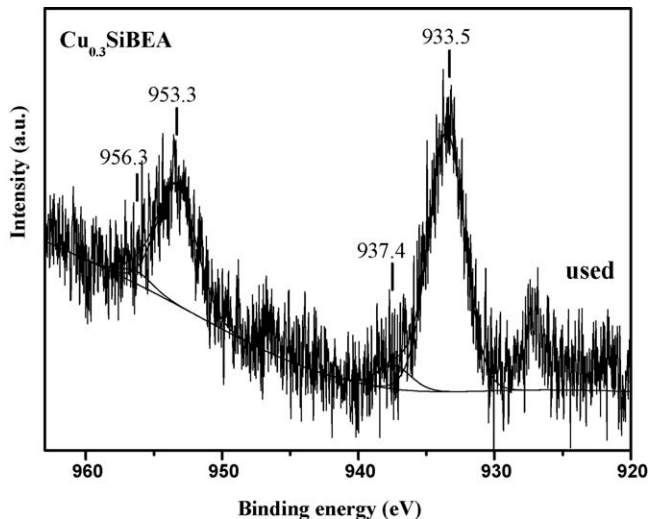


Fig. 3. XP spectrum recorded at room temperature of Cu 2p core level of used $\text{Cu}_{0.3}\text{SiBEA}$.

reduction could occur under X-ray beam irradiation. The experiments performed on Cu_xSiBEA samples irradiated even over 6 h have not evidenced any significant change in the XP spectra (not shown here). These results can be considered as a proof of lack in reduction of Cu(II) under X-ray irradiation.

Copper in Cu(II) oxidation state gives in general the shake-up satellite at electron binding energy of about 10 eV higher than the Cu 2p_{3/2} excitation, which is not observed for Cu(I) and Cu(0). Thus, this feature can be used to distinguish between Cu(II) and Cu(I) or Cu(0). The KE of Auger transition related to Auger parameter provides also an efficient tool to describe location and aggregation of Cu ions, as it was shown earlier for ZSM-5 [36–38], MCM-41 [38] and beta [34,38] zeolites doped with Cu.

The electron binding energy of certain element depends not only on its oxidation state but in most cases on its chemical environment. As shown in Figs. 3–5, Cu 2p spectra obtained for $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ are decomposed into two doublets taking into account the measurement resolution (less

Table 1

XPS chemical analysis of $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

Chemical composition (at.%)	$\text{Cu}_{0.3}\text{SiBEA}$		$\text{Cu}_{1.5}\text{SiBEA}$		$\text{Cu}_{3.3}\text{SiBEA}$		
	Used	Fresh	Used	Oxidized	Fresh	Used	Oxidized
C	3.1	4.9	5.9	1.8	4.5	3.9	3.4
Si	37.2	35.3	35.3	37.1	36.4	35.1	35.5
O	59.6	59.4	58.4	60.8	58.4	60.3	60.4
(OH, H ₂ O)	2.3	2.5	1.9	1.9	2.0	2.9	3.6
Cu/Si	0.0035	0.0087	0.0089	0.0086	0.0173	0.0180	0.0177

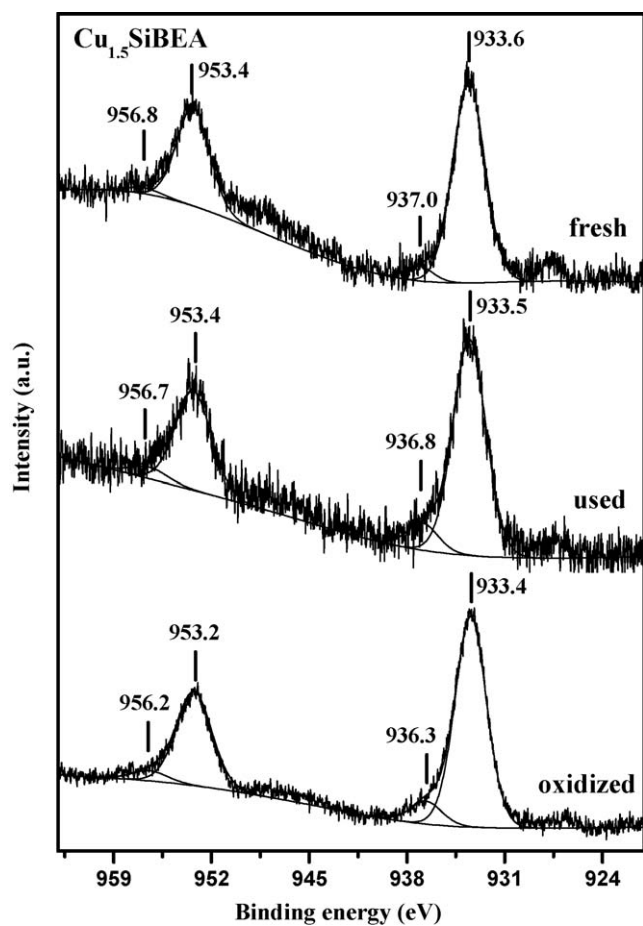


Fig. 4. XP spectra recorded at room temperature of Cu 2p core level of fresh, used and oxidized $\text{Cu}_{1.5}\text{SiBEA}$.

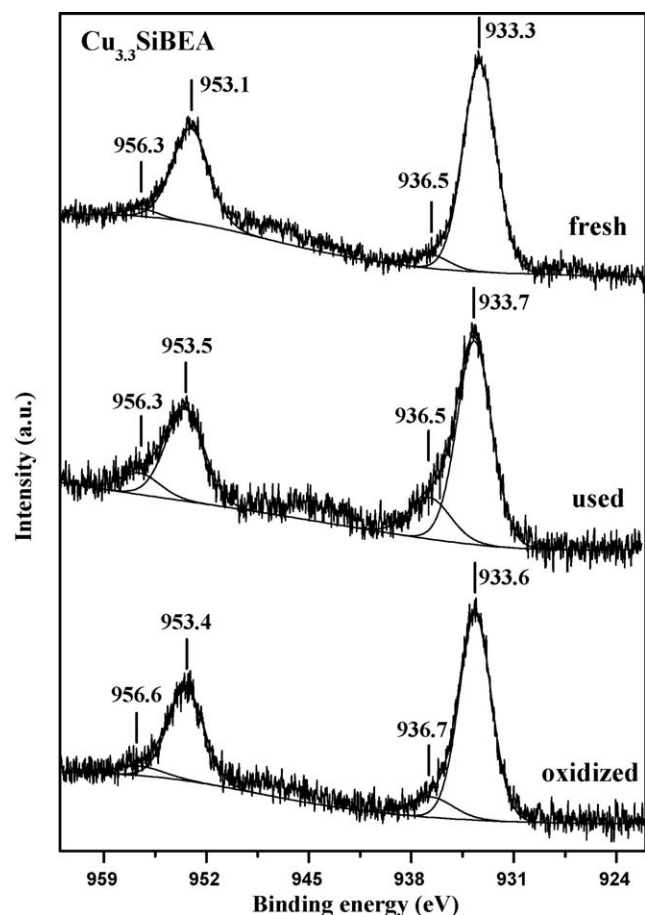


Fig. 5. XP spectra recorded at room temperature of Cu 2p core level of fresh, used and oxidized $\text{Cu}_{3.3}\text{SiBEA}$.

than 0.9 eV), type of excitation and chemical composition. For all samples, the most intensive peak of Cu $2p_{3/2}$ excitation shows the binding energy slightly higher than 933 eV and the second peak with energy above 936 eV.

As it is reported earlier by Zhou et al. [38] for Cu/ZSM-5 system, the series of XPS Cu 2p spectra were acquired and the BE of 933.2–933.4 were considered as related to Cu(II). Moreover, the shake-up satellite intensities were observed as being dependent on the type of the zeolite applied. The most intensive shake-up satellite of Cu(II) was observed for Cu/ZSM-5 and the lowest for Cu/Beta.

Moreover, Corma et al. [34] have reported that for Cu/Beta zeolites there is a relation between the Cu $2p_{3/2}$ binding energy and Auger parameters and the Cu chemical state. They showed the 'B' labeled region assigned to Cu(II) or Cu(I) in 'intra' positions of the Beta zeolites. The values of our parameters (BE and alpha) can be found inside that region suggesting that Cu(II) is present in our system. The Cu(II) species observed in ZSM-5 by Grunert et al. [36] appeared in much different region of BE indicating that copper-matrix interaction has stronger impact on Cu 2p BE than the oxidation state. In addition, when we refer to our previous works on Cu zeolites [17,18], in particular the Cu K-edge EXAFS and XANES data, they clearly indicate presence of Cu(II) ions in our system.

For better description of the copper species present in Cu_xSiBEA , we have compared the KE of Auger Cu L_3VV transition and modified Auger parameter (α') obtained for these samples with those appropriate for the reference compounds: Cu(0), Cu_2O and CuO. As shown in Table 2, the KE of Cu L_3VV transition is between 913.0 and 913.6 eV for Cu_xSiBEA samples and this is much lower

than that observed for Cu(0) (918.6 eV), Cu_2O (916.6 eV) and CuO (917.6 eV) [34,39–41]. Similarly, the values of modified Auger parameter (α') for Cu_xSiBEA are much lower (Table 2) than that observed for the reference compounds: 1848.8–1849.6 eV (Cu_2O), 1851.0–1851.4 eV (Cu(0)) and 1851.3–1851.7 eV (CuO). It shows that the Cu L_3VV transition and the modified Auger parameter for all Cu_xSiBEA are much lower than those observed for bulk values, suggesting that copper is present in highly dispersed phase (mainly as isolated Cu(II)) that is confirmed well by the studies of Cu/Beta zeolites [34].

In addition, the shake-up satellite associated with Cu $2p_{3/2}$ peak appearing at about 945 eV for $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ confirms that copper is mainly present in (II) oxidation state. The low intensity of the satellite for all Cu_xSiBEA is probably due to high copper dispersion in the zeolite structure as isolated tetracoordinated Cu(II) [34,38]. The presence of second component (B) for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ at higher BE of about 936–937 eV and 956–957 eV, respectively, reveals that probably some amount of octacoordinated Cu(II) species is also present, which is in line with similar studies on Cu/Y zeolite reported by Narayana et al. [42].

Moreover, for all Cu_xSiBEA zeolites after SCR process (used Cu_xSiBEA) and after further treatment in air at 773 K (oxidized Cu_xSiBEA) (Table 2), a presence of a very limited or the lack of modification of Cu L_3VV transition followed by almost constant value of the α' parameter indicate that copper oxidation state as well as the Cu coordination in the zeolite matrix remains the same. It is confirmed by a small decrease of the Cu 2p intensity ratio of the peaks with BE close to 933 and 936 eV for $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ (Figs. 4 and 5) after SCR reaction and further treatment

in flowing air at 773 K and by absence of changing of intensities of the shake-up satellites related to the presence of Cu(II).

In conclusion, the XPS results indicate that only a little change in surrounding of copper in the Cu_xSiBEA catalyst occurs upon SCR of NO. It shows evidence of a relatively strong interaction between Cu(II) and oxygen in the zeolite matrix. Furthermore, it confirms that copper is incorporated into vacant T-sites of SiBEA zeolite (Scheme 1) and it is mainly present as isolated tetracoordinated Cu(II). However, there is a certain probability that the large peak at about 933–934 eV is due to unresolved component containing of two kind of Cu(II) species. This does not exclude the possibility that the peak at about 936 eV is related to octacoordinated Cu(II) in framework and/or extra-framework position, in line with earlier report [35]. However, the amount of latter species is relatively low for all Cu_xSiBEA samples as suggested by a little intensity of the equivalent peak. Moreover, the BE of Cu $2p_{3/2}$ close to 933–934 eV and the KE of Cu L_{3VV} transition close to 913 eV for used $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$, which are much lower than that appeared for reference compound containing Cu(I) and Cu(0) [34], suggest that main amount of copper is present as tetracoordinated Cu(II).

3.3. Catalytic activity of Cu_xSiBEA zeolite in the SCR of NO

As it was earlier reported [20], dealuminated SiBEA shows very low activity and NO conversion that does not exceed 7% in the whole temperature range (573–773 K). The high ethanol conversion reaching 90% at 623 K is mainly due to dehydration of ethanol but not to alcohol oxidation. However, the maximum yield of N_2 for SiBEA reaches only 5% at 675 K (result not shown).

The incorporation of Cu in the SiBEA leads to obtain a more active material, as shown in Fig. 6 where the conversion of NO on three Cu containing SiBEA zeolites are compared in SCR of NO by ethanol. For $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$, a substantial increase of the SCR of NO activity is observed with a maximum NO conversion of 33% ($\text{Cu}_{0.3}\text{SiBEA}$), 45.5% ($\text{Cu}_{1.5}\text{SiBEA}$) and 50% ($\text{Cu}_{3.3}\text{SiBEA}$) (Fig. 6) and yield of N_2 reaches 26%, 35% and 42.5%, respectively (Fig. 7).

For all copper containing Cu_xSiBEA , the ethanol conversion attains 100% conversion already below 573 K and only very small amounts of mild oxidation products (ethene, CO and other organic products) appear, much lower than that observed for Co_xSiBEA [20]. It points out that Cu_xSiBEA catalysts are more active than Co_xSiBEA in promoting the total oxidation of organic products, probable intermediates of the SCR of NO with ethanol, what

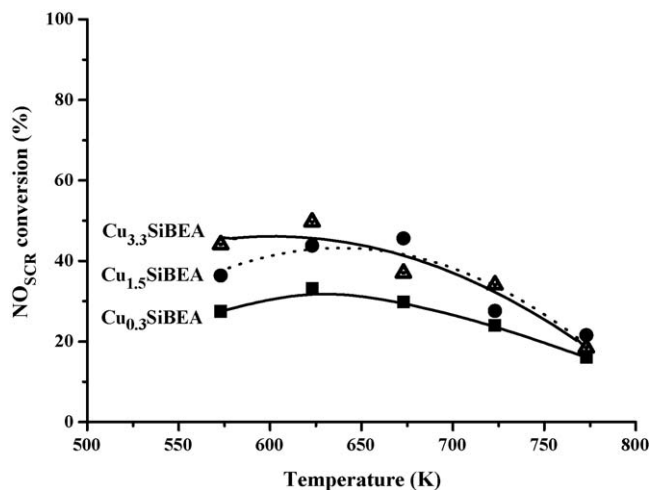


Fig. 6. Temperature-dependence of NO conversion in SCR of NO by ethanol on $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

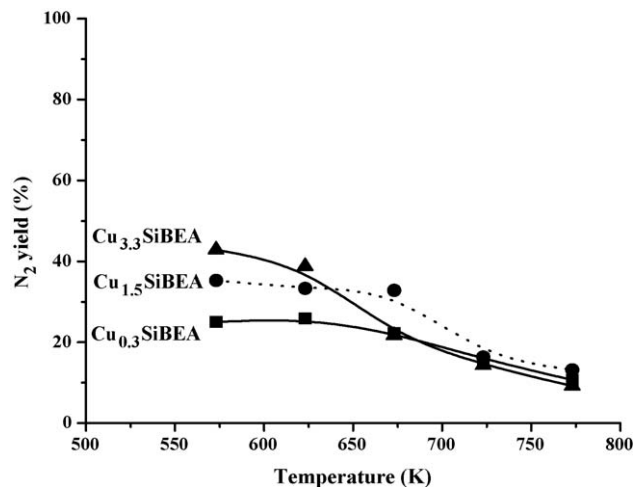


Fig. 7. Temperature-dependence of N_2 yield in SCR of NO by ethanol on $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

reflects their lower NO conversion level comparing to that observed on Co_xSiBEA catalysts [20].

These results confirm that the presence of copper ions in the framework of zeolite is necessary to promote the activity in the SCR of NO. The activity of Cu_xSiBEA in the SCR process increase with Cu content and the main reaction route is the reduction of NO toward N_2 . For $\text{Cu}_{0.3}\text{SiBEA}$, the selectivity toward N_2 exceeds 70% in the whole reaction temperature range between 573 and 773 K (Fig. 8). The selectivity toward NO_2 is close to zero at low reaction temperature (<600 K) (Fig. 9) but increase with reaction temperature up to 30% at 773 K, indicating that at higher temperature the level of NO oxidation into NO_2 on $\text{Cu}_{0.3}\text{SiBEA}$ is higher than that observed on the cobalt containing SiBEA (<15%) with the same metal content (0.3 Co wt%) [33].

The $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$ samples, exhibits also a high selectivity toward N_2 , which exceeds 50% in the whole reaction temperature range between 575 and 775 K (Fig. 8). As shown in Fig. 8 the selectivity toward N_2 over both samples decreases gradually from 100% and 75% to 55% and 50%, respectively, when the reaction temperature increases from 573 to 773 K. Simultaneously, oxidation of NO towards NO_2 over both samples increases from 0% and 20% to 35% and 50%, respectively.

It seems that similar behaviour of Cu_xSiBEA samples with different Cu content in SCR of NO by ethanol is likely due to the

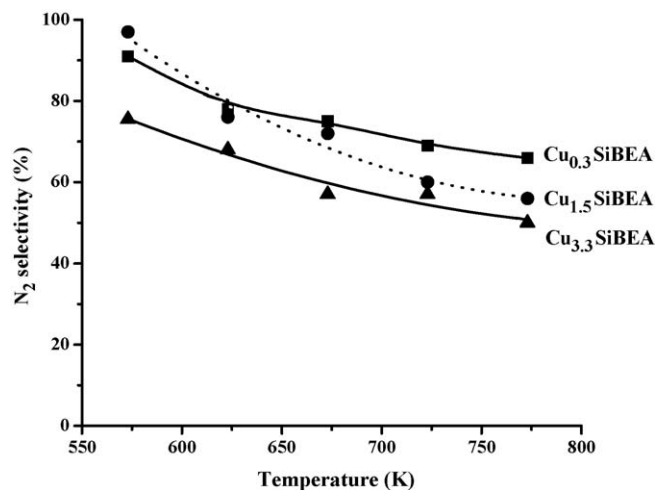


Fig. 8. Temperature-dependence of N_2 selectivity in SCR of NO by ethanol on $\text{Cu}_{0.3}\text{SiBEA}$, $\text{Cu}_{1.5}\text{SiBEA}$ and $\text{Cu}_{3.3}\text{SiBEA}$.

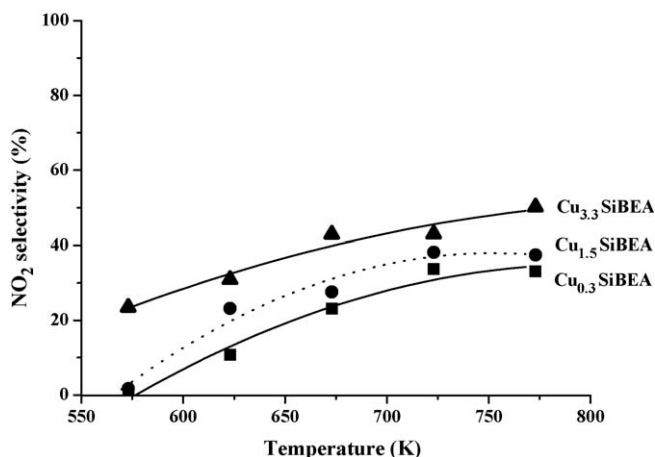


Fig. 9. Temperature-dependence of NO₂ selectivity in SCR of NO by ethanol on Cu_{0.3}SiBEA, Cu_{1.5}SiBEA and Cu_{3.3}SiBEA.

presence of similar copper species, isolated Cu(II) in tetrahedral coordination, as evidenced by UV–vis–NIR and XPS investigations. We suggest, that some decrease of selectivity toward N₂ and increase of selectivity toward NO₂ with Cu content, particularly on Cu_{3.3}SiBEA sample is related to the presence of small amount of other type of copper species, probably Cu(II) in octahedral coordination, in framework and/or extra-framework position, as suggested by XPS investigation.

It should be emphasised that the SCR activity of the investigated Cu_xSiBEA samples measured as $\ln(1 - X_{\text{NO}})$ with X_{NO} conversion of NO at 525 K does not increase linearly with Cu content (Fig. 10). Moreover, the $\ln(1 - X_{\text{NO}})$ vs Cu wt% plot extrapolated to the zero copper content do not pass through the origin of coordinate system. Such correlation may suggest that the first reaction order approximation can not be applied to the results and the relative activity of Cu_xSiBEA in SCR of NO decreases with the increase of copper content in the catalyst. It suggests that properties of copper ions incorporated into BEA zeolite change with Cu content and probably depend on the location of these ions in zeolite structure. It is probable that for low copper content (Cu_{0.3}SiBEA sample) Cu ions are mainly located in the one kind of framework sites and for higher copper content (Cu_{1.5}SiBEA and Cu_{3.3}SiBEA samples) Cu ions are located in the two kinds of framework sites, however mainly in second one, as we have mentioned above during consideration of XPS results. It seems that the latter ions are less active in SCR of NO process.

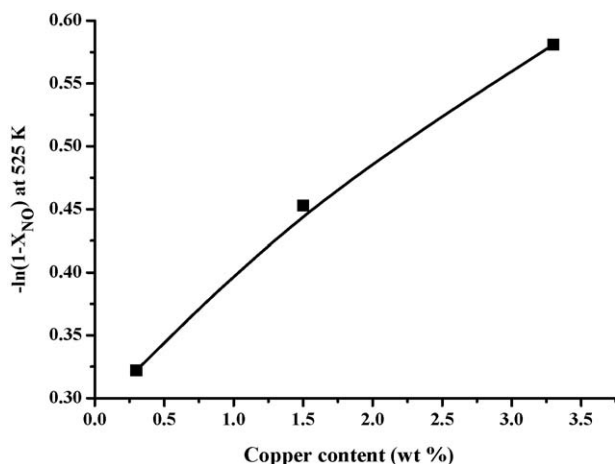


Fig. 10. Dependence of NO conversion (X_{NO}) on Cu content of Cu_xSiBEA.

The data reported here show that the activity of Cu_xSiBEA in NO oxidation to NO₂ does not necessarily imply SCR activity, as it has been postulated earlier by several authors [43,44]. The less NO oxidation is favored (Fig. 9), the more SCR of NO toward N₂ on Cu_xSiBEA occurs (Fig. 8). According to our previous work [20] and literature data [43,45,46], it is likely that the reaction mechanism involves the preliminary adsorption of NO that is oxidized by O₂ forming an adsorbed NO_x species ($x = 2,3$) bound to a Cu(II) center. Framework Cu(II) ions present in Cu_xSiBEA zeolite could activate ethanol by a abstracting a hydrogen atom and then forming an N-oxygenated intermediate. This active intermediate is probably responsible for SCR of NO toward N₂ on Cu_xSiBEA catalysts, which in line with our earlier report on Co_xSiBEA [20]. At this moment the detailed information concerning mechanism of ethanol activated adsorption and nature of the active N-complex are still obscure. The recent experimental data obtained by us shows that the nitroethane and acetonitrile adsorbed on Co_xSiBEA and Fe_xSiBEA zeolites are very active and selective in the NO conversion to N₂ and seems to be one of the most probable N-oxygenated intermediate.

The SCR of NO into N₂ and NO oxidation into NO₂ seem to be competitive reactions and the ratio of N₂/NO₂ depends on the rate constants of both reactions and on reaction temperature. If we consider that at low temperature, reaction rate between adsorbed (NO_x) species and the organic molecule or desorption of reaction product is rate determining step (r.d.s.), the secondary reaction between NO₂ (undergoing sequential adsorption) and adsorbed organic species has no effect on the overall kinetics but the N₂/NO₂ ratio depends on the kind of Cu(II) species present in Cu_xSiBEA zeolite.

NO₂ appears mainly among the SCR products at high temperature range (Fig. 9), when the organic molecules were totally consumed by SCR process and thus oxidation of NO into NO₂ may occur. However, it seems that gaseous NO₂ is not involved in the SCR process. This suggestion is in line with earlier report of Burch et al. concerning oxide systems [45] and investigation of Grünert and co-workers [47,48] and Stakheev et al. [49] on zeolite systems. In the latter paper the authors postulated that on Co-ZSM-5 zeolite with isolated Co sites gaseous NO₂ does not participate in the SCR process.

Further investigations are undertaken to better describe of the Cu sites in Cu_xSiBEA zeolites active in SCR of NO by *in situ* photoluminescence, EPR and FTIR spectroscopy of adsorbed CO and NO.

4. Conclusions

The objective of this work was to investigate the effect of the copper content on the activity of Cu_xSiBEA zeolites in SCR of NO by ethanol.

The combined use of XRD, DR UV–vis–NIR and XPS gives evidence that copper incorporated in SiBEA zeolite by the two-step postsynthesis method described earlier [17,18] is present mainly as isolated tetracoordinated Cu(II). The incorporation of Cu into the vacant T-sites of SiBEA is evidenced by XRD. The presence of Cu in the (II) oxidation state and in tetrahedral coordination in all Cu_xSiBEA samples is evidenced by DR UV–vis–NIR and XPS investigations.

Cu_{0.3}SiBEA, Cu_{1.5}SiBEA and Cu_{3.3}SiBEA with tetracoordinated Cu(II) are active in SCR of NO by ethanol with the maximum NO conversion at 573 K of 33%, 45.5% and 50% and selectivity towards N₂ of 90%, 97% and 75%, respectively. These results indicate that the SCR of NO occurs on isolated tetracoordinated Cu(II), without the presence of Al atoms, which have been removed from the zeolite structure upon acid nitric treatment as shown in Scheme 1.

The activity of Cu_xSiBEA in the SCR process increases with Cu content and the main reaction route is the reduction of NO toward N₂. The decreases of selectivity toward N₂ and increases of selectivity toward NO₂ with Cu content, particularly on Cu_{3.3}SiBEA is probably related to the presence of small amount of octacoordinated Cu(II), in framework and/or extra-framework position, as suggested by XPS data.

The possible pathway of formation of tetraordinated Cu(II) in the framework of Cu_xSiBEA is proposed as well as the different steps in SCR of NO by ethanol.

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